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Electroless Deposition of Nanocomposite NiP-Coatings on Metal Substrates

1. INTRODUCTION

In the recent years electronics and electrical engineering have faced the problem how to coat dielectrics (glasses, ceramics, polymers), semiconductors and metals difficult to be coated (aluminium and magnesium alloys, titanium, tungsten, molybdenum, etc.). Simultaneously the requirements towards uniformity of metal coatings and their characteristics such as hardness, resistance against corrosion, wear hardness, coefficient of friction etc., are constantly increased.

Chemical nickel plating on aluminium and many of its alloys is applied with a view to improve the surface hardness, corrosion protection as well as to provide possible welding. Many authors deal with the chemical nickel plating on aluminium due to the relatively low price of aluminium and its alloys and the above mentioned reasons. By these reasons and the relative low price of its alloys the electroless nickel plating on aluminium from many authors was studied.

It is suggested in [1] that aluminium without its protective oxide layer is much more electronegative due to which nickel nuclenses are deposited on its surface. They act as catalysts on the formation of the nickel-phosphorus coating. This manner of work is relatively simple but not reliable since the plated Ni coatings have weak adhesion to the base material.

According to D.Stoychev et al [2-5] the main process in the methods for deposition of galvanic coatings on aluminium developing in the recent years is the so-called “Preliminary immersion treatment”. The latter allows to remove the natural oxide layer on the aluminium surface and simultaneously to deposit a thin zinc or tin layer. It is possible to further successfully deposit on this intermediate layer various coatings of required adhesion.

Lately chemically nickel plated details have been often applied in the technique. A hard and bright chemical nickel coating can be deposited on steel, aluminium, copper and

copper alloys. “Soft” materials such as aluminium can be protected against external impact through deposition of a hard nickel. Steel is the most often used base material due to its good mechanical characteristics (hardness). Aluminium competes with steel from economical point of view. Sycyzgiel [6] suggests to apply a coating of chemically deposited nickel with SiC as a protection against wearing.

It can be noticed in the cited literature that only a few papers deal with preparation of dispersion coatings on some metals such as titanium, nickel, etc. That is why the present work aims at studying the preparation of NiP- and dispersion NiP-coatings on different metals without preliminary activation.

2. EXPERIMENTAL

The investigations were carried out with sample plates of aluminium, iron, titanium and nickel. The electroless deposition of dispersion NiP-coatings was performed according to two technological schemes, namely, with and without ion activation.

Etching was carried out with different solutions depending on the substrate. Chemical nickel plating was carried out in an acid electrolyte with pH 4,6 – 4,8 and temperature 82^{o}C and varying deposition time. The main components of the base electrolyte were nickel sulphate and sodium hypophosphite. Complex forming agent, buffer substances stabilizers, etc were added as well. The electrolyte was stirred with a magnetic stirrer with 300 rpm.

TiO_2, Al_2O_3, SiO_2 nanoparticles (powders) with grain size of 30 to 60 nm were used as dispersoids. The deposition rate of dispersion coatings was determined gravimetrically by the thickness of the coatings produced. Changes in morphology were followed with T200 SEM, Jeol, Tokyo. The content of incorporated particles was determined by X-ray quantitative micro probe analysis.

3. RESULTS AND DISCUSSION

It is known that the surface to be chemically nickel-plated should act as a catalyst. The nickel layer continues to grow after the base metal has been completely covered, since nickel itself catalyzes the deposition [1].

Our investigations reported in [7] reveal that it is advisable to use a new generation of activating solutions based on complex palladium sulfate ions. We have tested them as well on other metal substrates, namely, aluminium, iron, titanium and nickel.

It is seen in Table 1 that the thickness of NiP-coatings deposited in the presence and in the absence of ion activator do not differ significantly except for aluminium on which the thickness of the coating deposited in the absence of activator is higher. The possible reason for this is the big difference in potentials of Ni and Al.

Table 1

Substrate	Thickness of the NiP-coating in the presence of ion activator, μm	Thickness of the NiP-coating in the absence of activator, μm
Aluminium	11.22	14.58
Iron	12.10	11.88
Titanium	11.88	12.10
Nickel	15.84	12.76

It should be noted that after activation the deposition rate of nickel coating on aluminium, steel and titanium is almost the same. The following immersion reaction occurs due to the difference in the electrode potentials of the base metal and palladium:

$$Me + Pd^{2+} = Pd + Me^{n+}, \quad \text{where Me = Al, Fe, Ti}$$

This reaction produces palladium, which also exerts catalytic action on chemical nickel plating.

From economical point of view our further experiments were carried out of substrates in the absence of activator.

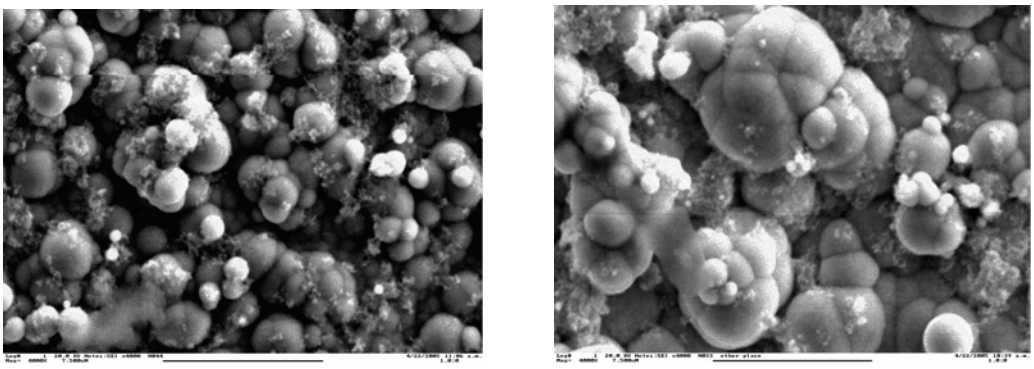
Data summarized in Table 2 show the change in the thickness of the pure NiP-coating on Al, Fe, Ti and Ni and the change in thickness of dispersion NiP—coating in the presence of nanoparticles (TiO_2, Al_2O_3, SiO_2). It is seen that dispersion coatings with TiO_2 are much thicker than the pure NiP-coatings and that with other two dispersoids (Al_2O_3, SiO_2). The thickness of dispersion coatings with Al_2O_3 and SiO_2 does not differ significantly from that of the pure NiP-coating.

Table 2

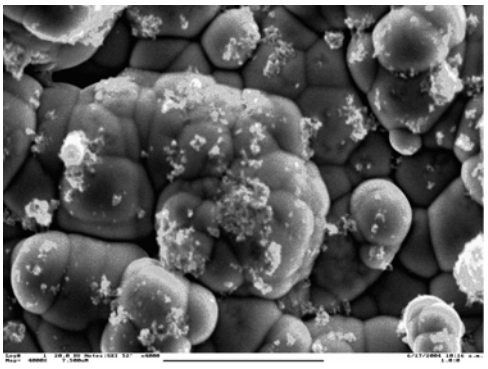
Substrate	Thickness of the NiP-coating without activator, μm	Thickness of the NiP+2.5g/l TiO_2 coating, μm	Thickness of the NiP+2.5g/l Al_2O_3 coating, μm	Thickness of the NiP+2,5g/l SiO_2 coating, μm
Aluminium	14.58	18.51	12.90	15.14
Iron	11.88	15.18	11.44	11.88
Titanium	12.10	16.06	13.42	11.66
Nickel	12.76	12.10	14.51	13.58

Fig.1 demonstrates SEM photographs of surface morphology of NiP+ 2.5g/l TiO_2 coatings deposited on Al substrate at different deposition time - 10 , 20, 60 min. At deposition time of 10 min one can still observe separate TiO_2 particles covered with about 2.5 μm NiP. At longer deposition time a dispersion coating about 8-times thicker is present in which agglomerate formations are dominating (60 min), the latter determining a much more rough structure.

The change in thickness of the NiP-coating and in Ti content in the coating are studied as a function of TiO_2 in the electrolyte (Fig.2). It is seen that a weak reduction of the thickness is observed with increase in the TiO_2 concentration up to 2,5 g/l and an insignificant enhancement further on. With 1 and 2.5 g/l TiO_2 the amount of incorporated Ti is almost the same. With further increase in TiO_2 concentration in the base electrolyte the number of retained particles on agglomerates is increased. The latter are blocked to a greater degree at 5 g/l TiO_2 and higher concentration which negatively affects the autocatalytic action of Ni on the base Redox process running in the electrolyte hence the thickness of the coating is not noticeably changed. Our further experiments were carried out with concentrations of 2.5 g/l of studied dispersoids. With this concentration maximum incorporation of particles in the dispersion coatings is achieved and the thickness is sufficiently high.



10 min 20 min



60 min

Fig.1 SEM photographs of the surface of NiP-TiO_2-coating at different deposition time (82^{o}C, 45 min) (x4000)

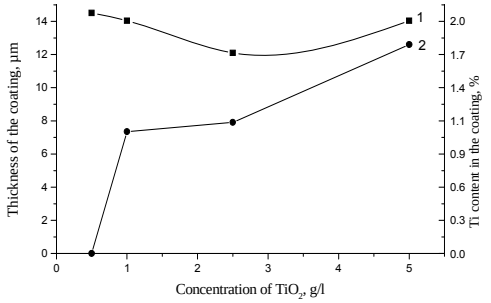


Fig.2 Thickness of a NiP-TiO_2-coating and Ti content in it as a function of TiO_2 concentration in the electrolyte: curve 1 – thickness of the coating; curve 2 – Ti content in the coating (82^{o}C, 45 min)

Table 3 summarizes data about thickness and TiO_2 content in NiP-coatings deposited on different substrates. Comparing the results one can see that the thickness of the dispersion coating deposited on aluminium is the highest as compared to other substrates. On the other hand, comparing only data about aluminium substrate with

different disperse particles it is established that the thickness in the presence of TiO_2 is the highest (18.51μm). Among studied dispersoid (Al_2O_3, SiO_2, TiO_2) the greatest incorporation is observed with Al_2O_3 (1.64%Al).

Table 3

Substrate	Thickness of the coating, μm	Ni contents in the coating, %	P content in the coating , %	Ti content in coating, %	Oxygen content in the coating, %
Aluminium	18.51	95.03	3.14	1.1	0.74
Titanium	16.06	94.73	3.42	1.11	0.74
Iron	15.18	95.20	3.00	1.08	0.72
Nickel	12.10	92.22	4.96	1.69	1.13

Interesting results have been obtained in experiments aiming at preparation of a better dispersion coating on a nickel substrate. Due to the running autocatalytic process we have to study different etching solutions in the presence and in the absence of ion activator (Table 4) It is seen that dispersion coatings deposited without activation are less thick than those with activation.

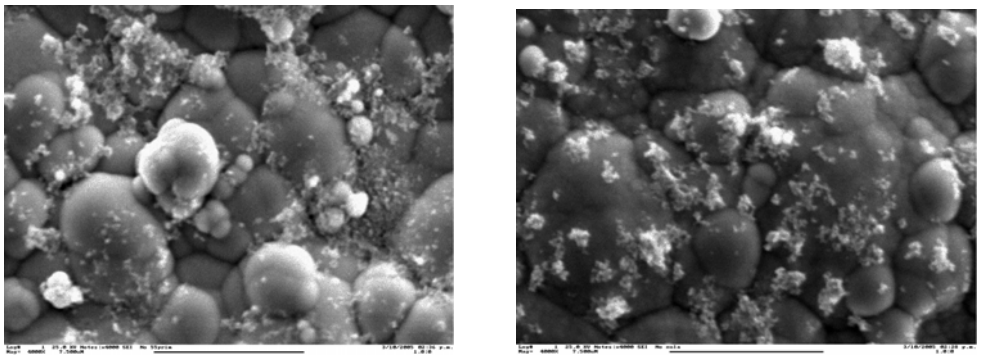
Table 4

Coating	Etching	Activation	Thickness of the coating, μm	Ti % (Al)
NiP	Ammonium persulfate	Yes	15.84	-
NiP+TiO_2(2.5g/l TiO_2)	1:1 HCl	Yes	16.5	0.76
NiP	1:1 HCl (60^oC)	No	12. 6	-
NiP+TiO_2(2.5g/l TiO_2)	1:1 HCl (60^oC)	No	12.10	1.69
NiP+Al_2O_3(2.5g/l Al_2O_3)	1:1 HCl (60^oC)	No	14.51	1.63%Al

On SEM photographs on Fig.3a and 3b are shown dispersion coatings with 2.5g/l TiO_2 deposited on a nickel substrate in the presence and in the absence of activator, respectively. Fine, densely situated particles of the forming dispersion coating are observed on the surface (Fig.3a). These are the sites on which a catalytically active palladium metal is produced in the course of activation. At prolonged time of nickel plating these micro particles are grown up and are combined in greater or smaller

agglomerates, respectively.

Fig.3b exhibits the role of the catalyst in the base redox process running in the electrolyte in the course of nickel plating. The NiP-TiO_2 ,micro particles formed are gradually coalesced in dense agglomerates.



a b

Fig.3 SEM photographs of NiP+2.5g/l TiO_2- coatings: a- after preliminary activation; b – without preliminary activation (x4000)

4. CONCLUSIONS

The preparation of NiP- and dispersion NiP-coatings with nanosized dispersoids Al_2O_3, SiO_2, TiO_2 on different metal substrates (Al, Fe, Ti, Ni, Cu) is studied. It is established that dispersion coating of good quality can be produced without special activation with palladium salt. Activation is required only for copper substrates. At that the base metal in a pure state catalyze the deposition. The optimum conditions for the preliminary treatment of metal substrates (Al, Fe, Ti, and Ni) are established. Original methods for nickel plating of these substrates are applied.

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